



A Study of the Effects of Water on the Electrochemical Properties and Characterization of Co-Zn Alloys from a Deep Eutectic Solvent

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Abstract

Co-Zn alloy coatings have been electrodeposited on steel in choline chloride (ChCl) based liquid in the presence of various concentrations of water. The conductivities of Co, Zn, and Co-Zn electrolytes were found to improve through enhancing volumes of water. The speciation of Co in a Co-Zn electrolyte was investigated using UV-visible spectroscopy. A negative shifting in the Co species was detected when water was added to Co-Zn solutions. The cyclic voltammetry was used to examine the redox potential of the plating solutions, from which it was found that when water was added to Co, Zn, and Co-Zn electrolytes. The redox maximum frequency rises and changes in a progressive direction. Scanning electron microscopy (SEM) was used to examine the morphologies of films. By enhancing the volume of water, the morphology of the deposited Co-Zn coating was found to change. The compositions of Co-Zn coatings made from the electrolyte with water were found to be 19.83 wt% Zn and 80.13 wt% Co. The roughness of the Co-Zn film deposit was reduced to about 7.642 nm when the deposition was achieved from a bath containing 20% water. The X-ray Diffraction (XRD) technique was involved to investigate the XRD pattern of the Co-Zn deposits.

Keywords: Electrodeposition; Co-Zn alloy; deep eutectic solvents; additives (water)

1. Introduction

Cobalt is a famous metal that has hard magnetic material and its alloys have been presented to processes excellent magnetic properties which are required for high-performance magnetic applications[1]. However, as a result of the narrow electrochemical potential window of water the electrodeposition of Co-Zn alloy in the aqueous solution is difficult. Therefore, the ionic liquids (ILs) that have large electrochemical windows are required as the supporting electrolytes for electrodeposition of Co-Zn alloys. From numerous ILs, the chloroaluminate-based ILs have been widely used for the electrodeposition of different alloys owing to Lewis acidity or basicity may able to be adjusted[2]. It has also been stated that the electrodeposition of cobalt-aluminum alloys from chloroaluminate ionic liquid, the composition and morphology of deposits depend on the applied potential. Katayama *et al.*[3] examined the influence of temperature on the electroplating of Co in ionic liquid in the presence of additives. By increasing the temperature, the excess potential for Co deposition was found to be diminished. A number of distinct room-temperature ionic liquids have been proposed as new method for

coating[4]. In ionic liquids, a number of investigations on the electrodeposition of Co have been reported. Co electrodeposited on the substrate had poor adherence [5-9]. Hygroscopic nature of these types has been investigated, as well as air- and water-stable urea and choline chloride melt. Relanie (choline chloride:urea) was the first deep eutectic solvent discovered by Abbott *et al.*[10]. It has been employed as a substitute fluid for certain metal electrodeposition processes [11-15]. Many deep eutectic solvents have good properties, for instance, non-toxic[16, 17], and their elements can be responsibly sourced, non-flammable, biodegradable, relatively affordable to synthesize, and can dissolve different metal oxides [18, 19]. Electroplating[12-14, 20-22], electropolishing[23], recycling of metal [24], desulfurisation and synthesis of polymer [25-28] are all domains where DESs are of great interest due to their particular physical properties. The complexes of Cu ions in Ethaline 200 with water was explored by Koen and Deun, who discovered that water can modify the species of copper ions in the based liquids [29]. Our own research group has examined the effect of water on the cobalt electroplating in the Ethaline 200 [7].

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A number of studies have been conducted to date on the characteristics of Co-Zn coatings deposited from aqueous electrolytes using various organic additives. However, electroplating of Co-Zn from DESs have not been studied. Here in this work, the effects of water on deposition and the nucleation process of Co-Zn deposit were examined from Ethaline 400 as based liquid. The physical and mechanical qualities of the Co-Zn alloys formed in this manner are significantly better than those obtained in waterless systems, and a brilliant Co-Zn alloy coating has been achieved. Co species present in Ethaline 400 were studied by UV-visible spectroscopy. Using cyclic voltammetry, the redox characteristics of the plating solutions were investigated. SEM/EDXS and AFM were used to disclose surface features such as morphology, alloy content, and roughness. XRD pattern of the Co-Zn deposits was investigated using the XRD technique.

2. Experimental

Choline chloride, $[\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{Cl}]$ (ChCl) (Aldrich 99 %) was recrystallized from absolute ethanol, filtered, and dried under vacuum. Ethylene glycol (EG) (Aldrich + 99 %), was used as received. The two components have been mixed by stirring (in a 1: 4 molar ratio of ChCl: hydrogen bond donor) at 60 °C until a homogeneous, colourless liquid form. The cobalt salts; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Aldrich ≥ 98 %) and the zinc salts; ZnCl_2 (Aldrich ≥ 99 %), were all used as received. The conductivity of the liquids was measured as a function of temperature and using different concentrations of water using a Jenway 4510 conductivity meter fitted with an inherent temperature probe (cell constant = 1.01 cm^{-1}). UV visible spectrophotometer: A Shimadzu model UV-

1601 spectrophotometer was used with the cell path length equal to 10mm. Values for λ_{max} were determined using the spectrophotometer's built-in peak-pick feature, using UV- probe software.

Cyclic voltammetry investigations were carried out using an Autolab/PGSTAT12 potentiostat controlled with GPES2 software. A three-electrode system was used, consisting of a platinum working-electrode (0.12 cm^2 area), a platinum flag counter-electrode, and a silver wire pseudoreference electrode. The working electrode was polished with $0.05 \mu\text{m}$ γ -alumina paste and cleaned by rinsing with deionized water followed by acetone prior to each experiment. All cyclic voltammograms were recorded at 70 °C and with a scan rate of $10\text{-}50 \text{ mV s}^{-1}$.

The electroplating was carried out on a mild steel plate in Ethaline 400 containing 0.5 M ZnCl_2 and 0.05 M CoCl_2 in both the absence and presence of water as shown in Figure 1. Dissolving MCl_2 (M = Zn, Co) in a 1:4 ChCl:EG-based liquid will form $[\text{MCl}_4]^{2-}$. Bulk electrolysis was carried out using cathodic plates (mild steel, $50 \text{ mm} \times 42 \text{ mm} \times 1 \text{ mm}$) which were mechanically polished and cleaned with acetone and rinsed with water, and dried. An iridium oxide-coated titanium mesh electrode, $40 \text{ mm} \times 50 \text{ mm}$, was used as an anode and prepared in the same manner. In all of the experiments, the solution temperature was 70 °C and deposition was carried out using a constant current for 1 hour, after which the substrates were removed from the solution and washed with water and acetone. The characteristic of surface was studied by scanning electron microscopy (SEM) while metals analysis of the plating compositions was performed by (EDAX). Powder X-ray diffraction technique was carried out to study XRD pattern of the Co-Zn deposits.

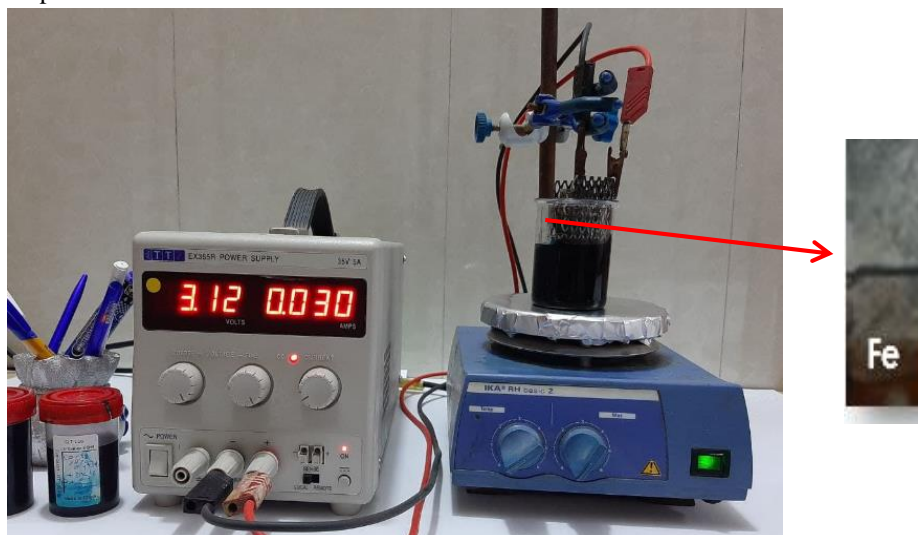


Figure 1. Image showing the electroplating apparatus.

3.Results and Discussion

The conductivity of Zn and Co in Ethaline 400 has a considerable influence on coating qualities in the metals electrodeposition from ionic liquids. Hence, it is necessary to investigate the conductivity of the Zn and Co solution. Fig. 2. demonstrates the conductivity of ZnCl_2 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and Co-Zn in Ethaline 400 as a function of temperature in the presence and absence of water. Here, the conductivities of the Zn, Co, and Co-Zn solutions were found to increase with increasing amounts of water for 20% that due to increase the number of ionic species (i.e H^+ and HO^-), while after addition more 20 % water that depresses the conductivities, this behavior attitude to elevate the crowded of the ionic atmospheres around the metals that needed to

deposit, as shown in Fig. 2a, 2b, and 2c, where clear increases in the conductivities of the Zn, Co, and Co-Zn electrolytes were observed. Furthermore, the conductivities of ZnCl_2 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and Co-Zn in Ethaline 400 containing 10%, 20%, and 30% water were investigated at different temperature (20 -80) °C as illustrated in (Fig. 2a, 2b, and 2c). The conductivities of Zn, Co, and Co-Zn solutions improved with enhancing temperature where this due to the concomitant increase in ionic movement, as seen in this figure, which is reliable with the preceding works [30-32]. The main goal of this section is to develop a system through enhance in conductivity that occurs when water is added. Because the amplitude of the contact amid the ions and water of the IL is slight compar to the ion interaction.

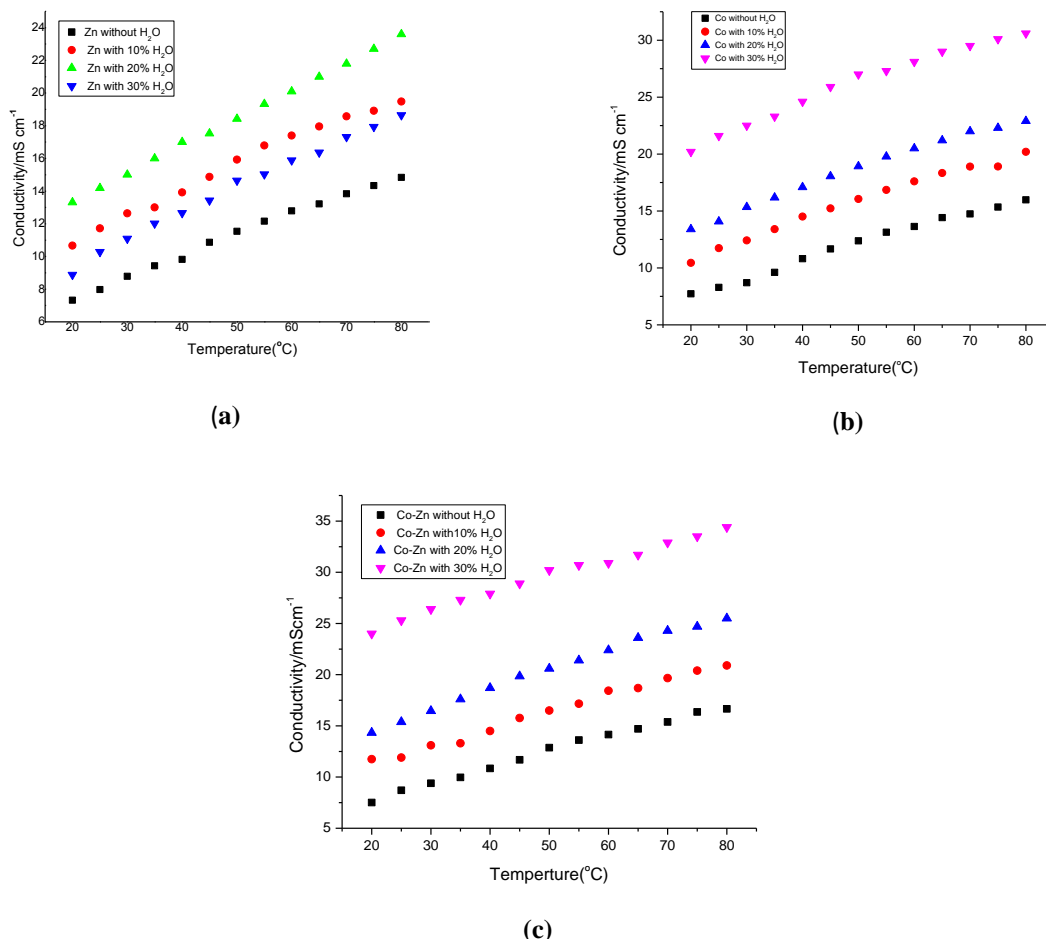
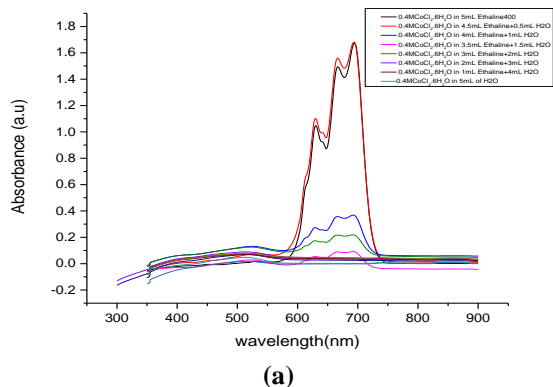


Figure 2. The conductivity of **a)** 0.3 M ZnCl_2 in Ethaline 400, **b)** 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400, **c)** 0.3 M ZnCl_2 and 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400, all measurements achieved at different temperature and various ratio of water.

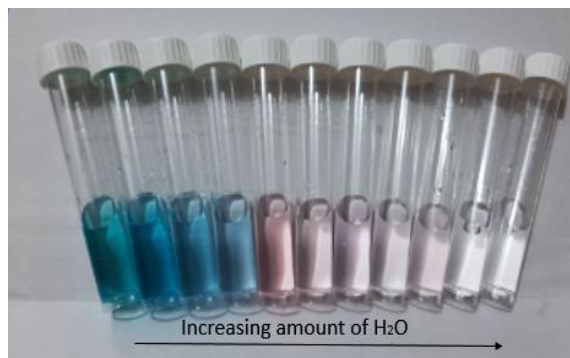
A. Speciation

In the presence and nonappearance of water, UV-Vis spectroscopy was utilized to identify $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ species in Ethaline 400. Figure 3a shows the UV-Vis spectra of 0.04 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solutions in Ethaline 400 in the presence and absence of different water ratios. The colour of 0.04 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400 was blue in the absence of H_2O . With the addition of increasing volumes of water, however, the colour progressively



(a)

changed from blue to light blue, then light blue to pink; the colour transforms from pink to colourless as the intensities of the peaks fade, as illustrated in Fig. 2b. The existence of $[\text{CoCl}_4]^{2-}$ complexes in the solution is indicated by the blue colour, i.e., peaks with pronounced intensity. Light blue and pink can be assigned to a mixture of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}_4]^{2-}$. It is clear from Fig. 2a that the colourlessness is indicative of the formation of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complexes.



(b)

(a) Photographic image of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400 with increasing amounts of H_2O , (b) UV-Vis spectra of 0.04 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400 with increasing amounts of H_2O .

B. Cyclic voltammetric (CV) studies

Using the cyclic voltammetry method, the redox of Zn, Co, and Co-Zn in Ethaline 400 were examined independently. Fig. 4. illustrates the individual cyclic voltammetric for 0.3 M ZnCl_2 and 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in Ethaline 400. Three electrodes were used in the experiments, which were conducted at 30 mV s^{-1} and at 70°C . In Fig. 4, the decrease of Co entities began around 0.6 V, whereas the oxidation existing high point for Co was about 0.2 V, which was lower than that found in Abbott *et al.*'s previous study of Co's electrochemical behaviour in Ethaline 400 [15]. The Zn species began to decline at 1.1 V, but the greatest oxidation current peak for Zn was at 1 V, according to the Zn voltammograms shown in Fig. 4. This conclusion is supported by Pereira *et al.*'s findings [33]. When the voltammograms of Zn and Co are compared, it is obvious that Zn species take more energy to decrease than Co species. This can be seen in Fig. 4, where Co began to decrease at 0.6 V and Zn at 1.1 V.

When a certain voltage is supplied, Co metal is first reduced on the electrode surface from a electrolyte holding Co and Zn ions. As can be observed in Fig. 3, Zn metal began to deteriorate at 1.1 V, while Co disbanding initiated at 0.2 V. This means that, in comparison to oxidizing Zn from the surface of electrode, Co metal requires a higher potential to dissolve. This suggests that Co has higher corrosion resistance than Zn, so Co employs in cathodic protection of Zn.

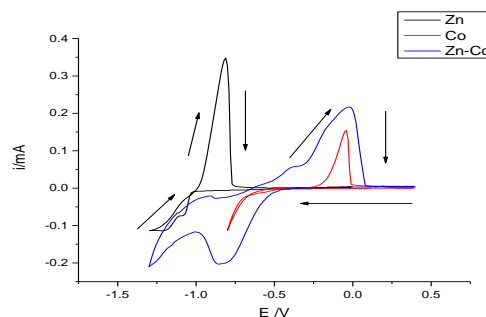


Figure 4. Cyclic voltammtry of 0.3 M ZnCl_2 and 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and Co-Zn in Ethaline 400 at 70°C , using a 30 mV s^{-1} scan rate

In the CVs of Ethaline 400 containing 0.3 M ZnCl₂ and 0.4 M CoCl₂.6H₂O, two deposition peaks are visible, as illustrated in Fig. 4. The first peak for deposition, which was detected at 0.8 V, coincides with Co deposition, while the second reduction peak, which was observed at 1.3 V, can be associated with Zn deposition. The anodic surface also has two peaks that begin at roughly 0.8 V and 1.4 V, respectively, which correspond to Zn and Co dissolution from the electrode surface, respectively. Two independent reduction peaks for Zn and Co were observed in the CVs of Ethaline 400 holding 0.3 M ZnCl₂ and 0.4 M CoCl₂.6H₂O at potentials identical to those previously observed for Zn and Co. As a result, it is not possible to deduce that a Co-Zn has made at first because this might merely be a co-deposition of Zn and Co; the XRD method was utilized in this work, as will be explained later.

A. Voltammetry of Zn, Co and Co-Zn alloy with/without H₂O

The influence of water on the cyclic voltammograms of Zn, Co, and Co-Zn in Ethaline 400 was investigated, as shown in Fig. 5, where increasing levels of water resulted in an increase in redox peak intensity of Zn, as shown in Fig. 5a. The same effect was noted in the redox peak of Co where clear increasing in the stripping and reduction peaks occurred with increasing concentration of water in the solution, as shown in Fig. 5b. This was due to the increase in conductivity of the solutions, as explained previously for Fig. 1. The oxidation-reduction of Co-Zn was also studied, in which can see the change in the redox potential of these metals with increasing amounts of water. The reduction potential shifted to more negative potentials with increasing amounts of water, and also enhancing in the stripping or desolation peaks of Co-Zn were detected, so that water can be seen to have an effect on the electrochemical properties of Co-Zn and reduction-oxidation. Moreover, the Fig. 5c demonstrates broad redox peak that due to electrodeposition of Zn-Co as alloy in all amount of using water and given more effect with using 30% water, that may be attributed to electrodeposition resistance after produced a alloy.

b. Effect of scan rate on voltammetry of Zn (II) and Co (II)

The effects of scan rate on the voltammetry of Zn, Co, and Zn-Co, as shown in **Figure 5** were studied, where it was found that the Zn and Co reduction peaks shifted cathodically with increasing scan rate; also, the intensities of these peaks increase with increasing the scan rate. The clear shift in Zn and Co deposition potentials (**Figure 6** (a) and (b)) with increasing scan rate might well be the result of the electrodeposition not experiencing any considerable effects of mass diffusion, with electron transfer or surface chemical reaction steps being the controlling mechanisms. The shift in Zn and Co deposition potentials obtained for our system could be due to resistive organic electrolytes, and it should be noted that the data shown in Fig. 6 that did not measure the resistance of the solution. In **Figure 6** (c), it reverses scans, double oxidation peaks appeared which correspond to the oxidation of pure Zn (Zn is oxidized in Ethaline 400 at about -1.5 V, as shown previously in Figure 4. The second stripping peak, which appeared at about -0.49 V, corresponds to the dissolution of pure Co.

c. Electroplating and properties of Co-Zn coatings

SEM was used to analyse the morphology of any metal deposits. Fig. 7 demonstrates a comparison of the morphologies of Zn, Co, and Co-Zn alloy films deposited from Ethaline 400. A pure zinc film with irregular pentagonal crystals and a pure Co coating with spherical agglomerates as a Broccoli shap, which are shown in the SEM images in Fig.7a and 7b, whilst Fig. 7c explains the Co-Zn crystallites that resemble rice grains, this experiments were performed using the Ethaline 400 to form all of the depositions on mild steel substrates at 70°C for 2 hours at a current of 30 mA. There is no doubt that the grain sizes of the Zn and Co deposits differ significantly. The morphology of the Co-Zn coating in the SEM deposit is shown in Fig. 7c, which differs markedly from that of pure Zn and Co deposits. This could be connected to changes in coating composition or electrolyte speciation. Because XRD (Fig. 9) may be involved to investigate the phase structure of the Co-Zn film, it may well represent the best tool for determining if this is an alloy or otherwise.

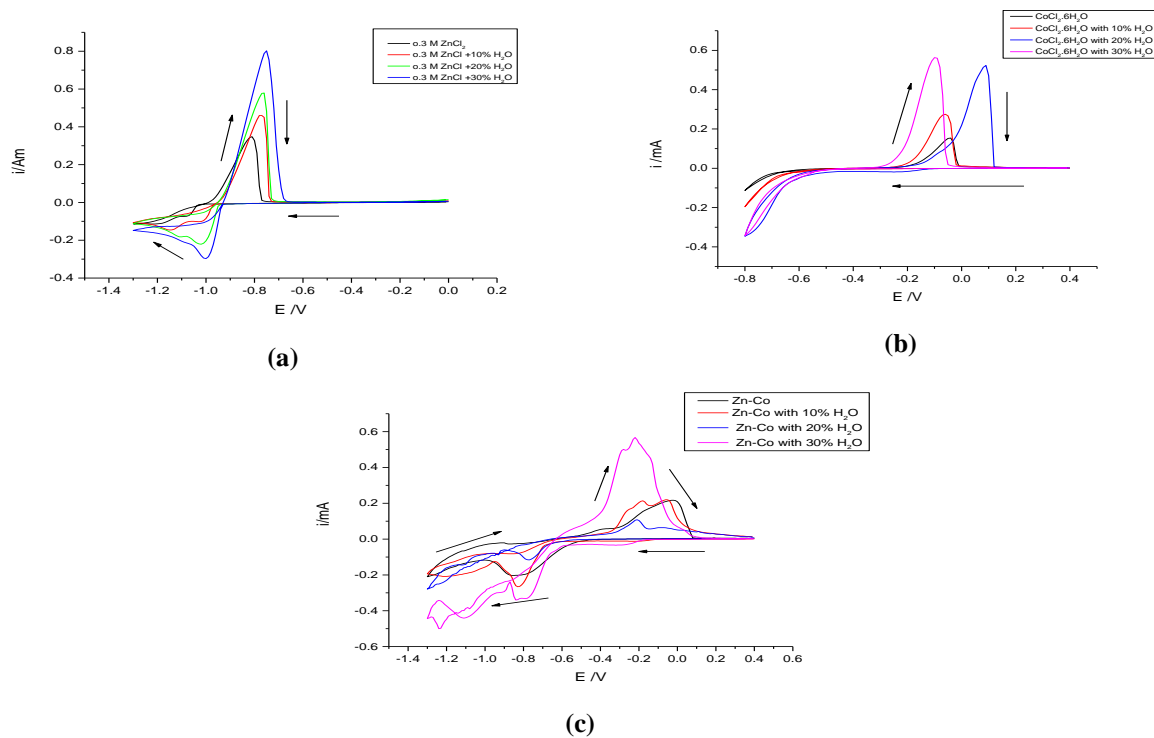


Figure 5. Cyclic voltammograms of Zn, Co, and Co-Zn produced by (a) 0.3 M ZnCl₂ in Ethaline 400 (b) 0.4 M CoCl₂.6H₂O, and (c) 3 M ZnCl₂ and 0.4 M CoCl₂.6H₂O in Ethaline 400 in the presence and nonappearance of water.

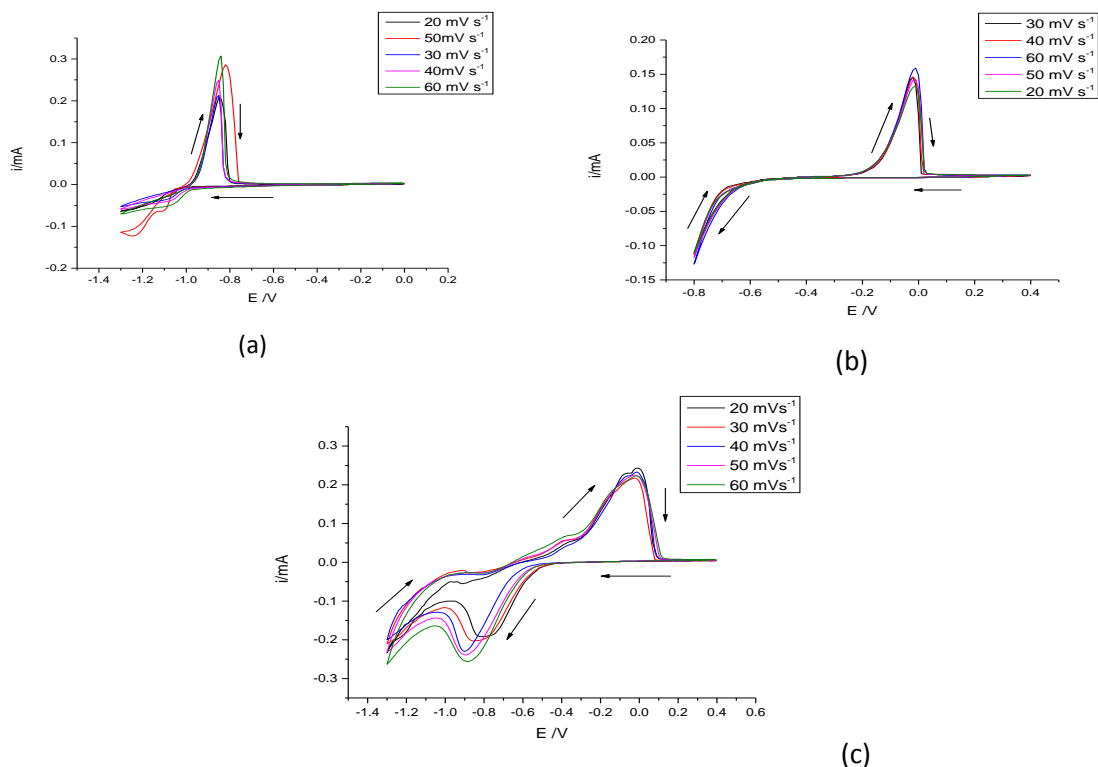


Figure 6. (a) Voltammetry of Ethaline 400 including 0.3 M ZnCl₂, (b) voltammetry for Ethaline 400 containing 0.4 M CoCl₂.6H₂O. (c) voltammetry for the electroplating of Co-Zn solutions.

c. Influence of water on the morphology of the Co -Zn deposits

Optical images, SEM, and AFM images of Co-Zn alloy deposits formed in an Ethaline 400 with 0.3 M ZnCl_2 and 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with and without various water concentrations are shown in Fig. 8. The morphologies of Co-Zn coatings has clearly different. The colour of the coating has been modified to be more vivid, as seen in Fig. 8c and 8d. This is a crucial approach for determining the nucleation and geography of metal coatings. In the absence and presence of water, AFM was used to study the topography and roughness of Zn, Co, and Co-Zn coatings from Ethaline 400. The results of the AFM and SEM are very similar. The deposition of Co-Zn coatings in a water-containing environment produces tiny grain sizes, particularly when the coating is obtained from a solutions in the precences 30% and 20% water. Addition, the rice shape for Co-Zn coating in absence water alters to textile shape with increasing the amount of water that cause raise the Zn wt % deposit (Table 2). This case can be interpenetrated to produce a small ionic atmosphere around Zn ion compared Co ion that beyond to Zn ion has a large ionic radus with low water ionic atmosphere hence the migrated of Zn ion from solution and deposit is being fast.

The roughness of the Co-Zn films was assessed via AFM. When electroplating was achived in the

attendance of 10% and 20% water, smoother Co-Zn deposits were created. The roughness of the Co-Zn deposits made by solutions with and of water is shown in Table 1. The Co-Zn deposit obtained in a waterless system had a roughness of 33.55 nm. Once the electroplating procedure was done in solution holding 10% water, however, the roughness of the Co-Zn deposit rose to 47.23 nm, and with a bath holding 20% water, the smoothness of the Co-Zn film deposit was reduced to about 8 nm, which represented a significant improvement. Water may act as a ligand in this case; as previously stated, some additives may be coordinated to the metal and make it harder to decrease, resulting in a flatter layer than would otherwise be possible in a system without water[34]. Based on results in table 2, the composition of the Co-Zn deposits obtained from water-containing systems has not changed particularly, i.e the summation of Zn % wt and Co% wt deposit are equal to 100%.

Moreover, the Zn % wt deposit elevates with increasing the water % , in contrast, the the Co % wt deposit depresses with increasing the water % that that attitude to the fast deposites of Zn ion happend compared with Co ion because Zn salt is not having water molecules in crystal lattice, hence it needed to low time to transfer from solution with less ionic atmosphere with water, and then deposit.

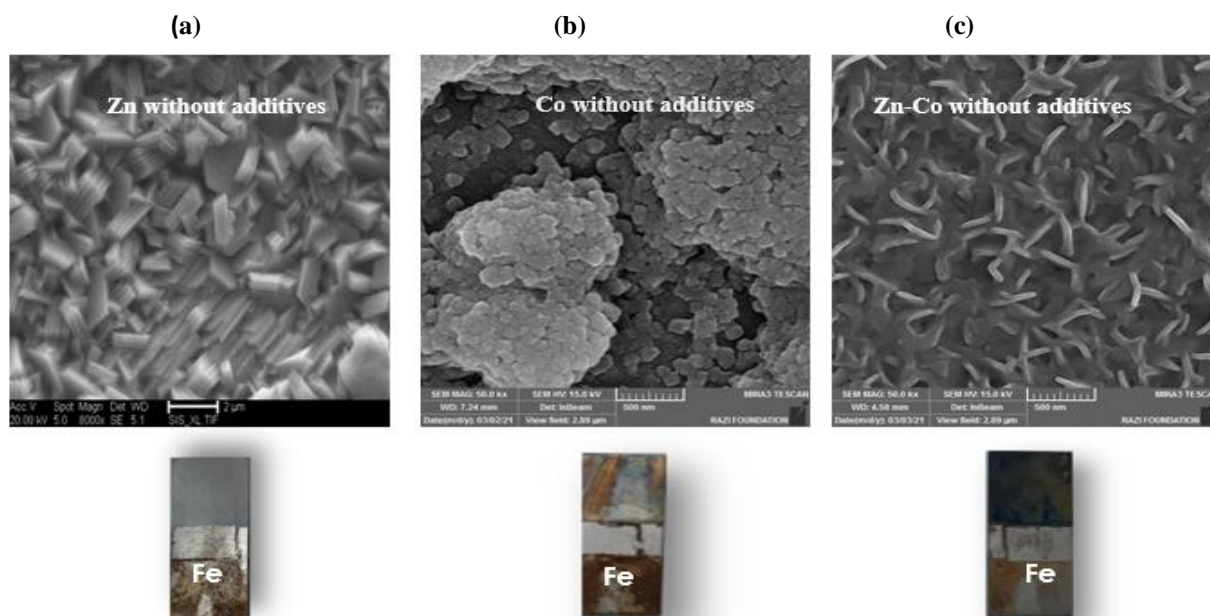


Figure. 7. SEM pictures after coating using (a) 0.3 M ZnCl_2 , (b) 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and (c) Co-Zn electrodeposition from Ethaline 400 containing 0.3 M ZnCl_2 and 0.4 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ without water.

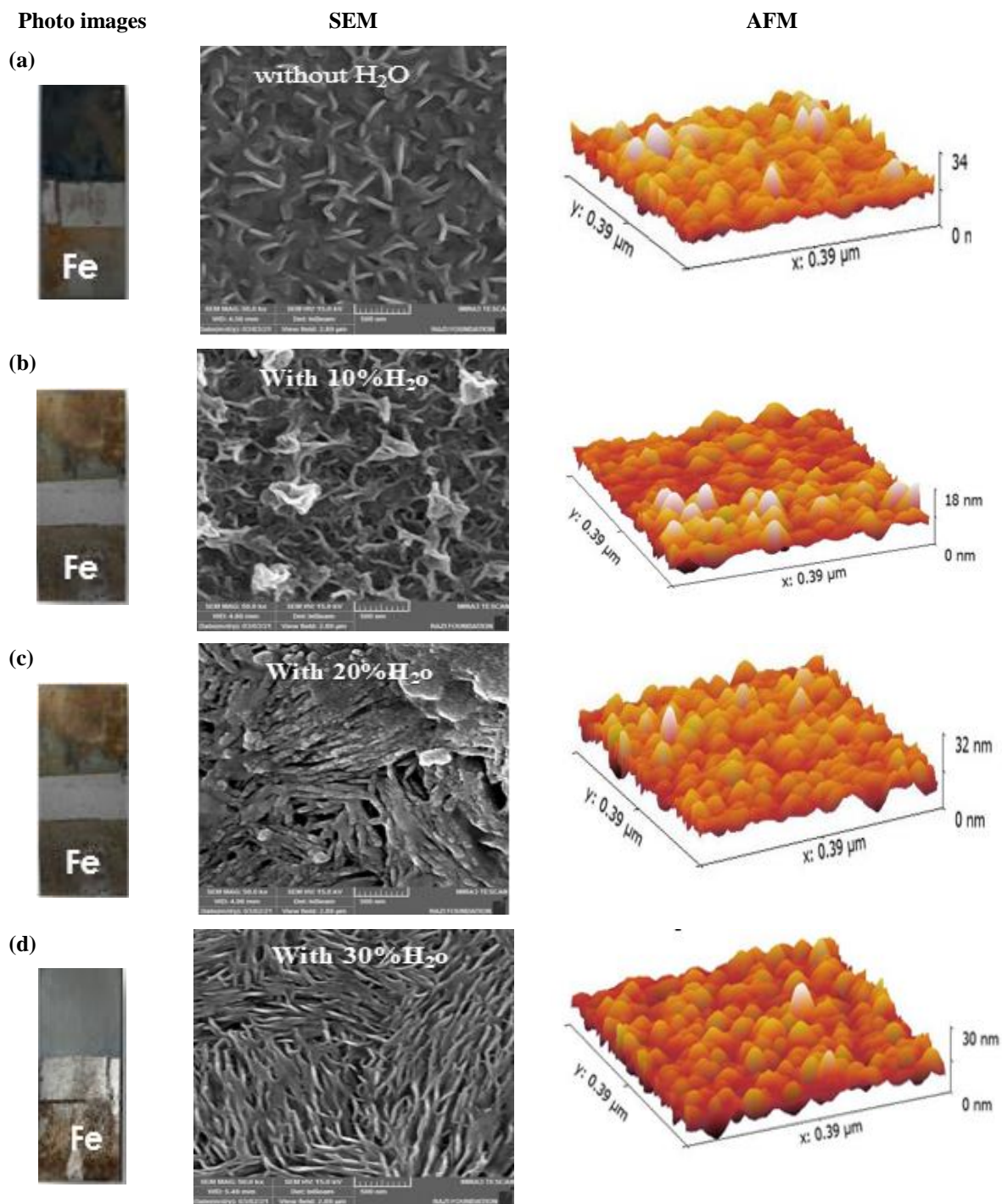


Figure 8. Morphologies and topography of Co-Zn electroplating in Ethaline 400 holding 0.4 M $ZnCl_2$ and 0.3 M $CoCl_2 \cdot 6H_2O$ in the attendance of (a) no water, (b) 10% H_2O , (c) 20% H_2O , and (d) 30% H_2O .

Table 1. In the presence and absence of water, the smoothness of Co-Zn films produced in Ethaline 400.

Metal salt	Additives (H ₂ O)	Roughness, Ra /nm	Average particle size/nm
Co-Zn	non	33.55	63.78
Co-Zn	10% H ₂ O	47.23	66.37
Co-Zn	20% H₂O	7.642	29.26
Co-Zn	30% H ₂ O	8.33	35.85

Table 2. The EDAX analysis results, when using ratio of Co-Zn films in the presence and nonappearance of water.

Co-Zn coating	Zn% Wt.	Co% Wt.
No water	19.83	80.13
With 10% water	30.42	69.58
With 20% water	57	43
With 30% water	77.3	32.7

G. X-ray diffraction

Figure 9 (a) shows the XRD patterns for pure hexagonal Zn, pure Co, Zn-Co deposits without water. All depositions were achieved from Ethaline 400 on a mild steel electrode at 70°C for 2 h using identical current densities. The (002), (100), (102), (103), (112) and (201) planes were observed in the pure Zn deposit with 2θ equal to 36.16°, 38.9°, 42.04°, 54.09°, 70.09°, 82.16°, and 86.56° [14,35], as shown in **Figure 9** (a), while the (110), (002), (101), (220), (110) and (200) planes were observed in the pure Co deposit at 2θ of 41.6°, 44.6°, 47.5°, 50.7°, 74.7°, 75.9°, and 90.5°, respectively. XRD patterns for Zn-Co deposits without water showed Zn planes, which were (002), (100), (102), (112), and (201). Co phases also were observed such as 44.6° and 47.5°, no specific shifting was observed in the XRD patterns of

the Zn-Co deposit derived from the electrolyte without water. In **Figure 9** (b), there are some signs of other phases which could be Zn-Co alloys, but these are extremely small compared with the pure metal phases. This indicates that a new phase has been formed in the deposition achieved from electrolytes containing water. Therefore, it can be suggested from XRD data that a Zn-Co alloy coating can be produced on a mild steel substrate from Ethaline 400 containing 0.3 M ZnCl₂ and 0.4 M CoCl₂.6H₂O at 70°C and a current equal to 30 mA.

Moreover, in figures 9a and 9b, the red shift in 2θ value 42.04° and 70.09° occurs to more values of 2θ after increases the amount of water and forms alloy that proved the produced metallic bond between Co-Zn as Zn-Co alloy, and Zn is deposited firstly then Co.

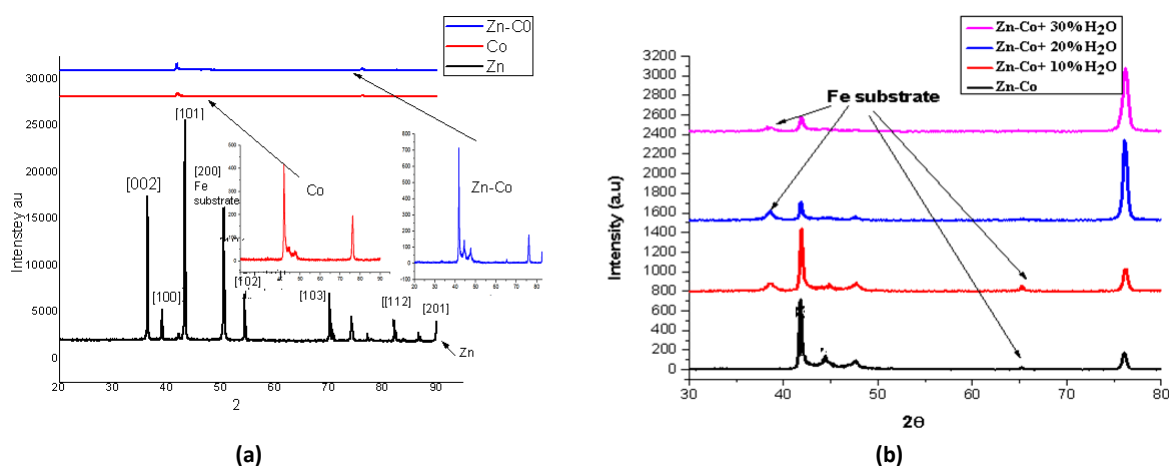


Figure 9. (a) XRD patterns of Zn electrodeposited, Co electrodeposited, and Co-Zn electrodeposited without water using 0.3 M ZnCl₂ and 0.4 M CoCl₂.6H₂O. B) XRD patterns of Co-Zn electrodeposited in Ethaline 400 by presencing of water.

4. Conclusion

This work demonstrated that a Zn-Co alloy film can be achieved from choline chloride/ethylene glycol (ChCl-Eg) based ionic liquid (Ethaline 400) containing 20% and 30% water. It has been found that the electrodeposition of Zn-Co alloys from Ethaline 400 in the absence of water will be unsuccessful. Increasing in the conductivities of the Co, Zn, and Co-Zn solutions have occurred with increasing amounts of water. The $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ speciation of Co was formed when water was introduced to the Co-Zn electrolyte. Voltammetry of Zn, Ni, and Zn-Ni was performed in Ethaline 500 in the absence and presence of water. Water coordinated to Co ions and inhibited the deposition of Co. Oxidation and reduction of Zn-Co peaks got bigger when the water was added to the plating bath due to increasing the conductivity of the solution. The morphologies of the Zn-Co deposit were improved when the deposition was achieved from an electrolyte containing water as additives. Moreover, it was found that the ratio of water affects the composition and morphologies of Zn-Co deposits where the percent of Co in the Zn-Co film reduced with an increasing amount of water in the bath. The roughness of Zn-Co film that formed from solution in absences of water was 33.55 nm while the roughness of coating decreased to be 8.33 nm when the deposition performed from an electrolyte containing 30% water. The XRD data was shown that the Zn-Co deposit shows that the diffraction peaks [101] and [103] were shifted toward more 2θ that proved the Zn-Co metallic bond happened, and the Zn is really deposited firstly then Co that regarded as cathodic protection for Zn deposit.

5. Conflicts of interest

“There are no conflicts to declare”.

6. Formatting of funding sources

Self

7. Acknowledgments:

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